

UDC 666.266.5:666.113.621'34'28

EFFECT OF IONS WITH DIFFERENT RADII ON THE PROPERTIES OF LITHIUM ALUMINOSILICATE PHOTOSENSITIVE DEVITRIFIED GLASSES

A. S. Krasnikov,¹ A. I. Berezhnoi,¹ and M. D. Krasnikova¹

Translated from *Steklo i Keramika*, No. 4, pp. 7–11, April, 1998.

The structure of strontium- and barium-containing lithium aluminosilicate photosensitive devitrified glasses and the effect of Sr^{2+} and Ba^{2+} on their dielectric loss is considered. It is established that in order to obtain a homogeneous compact microstructure and high physicomechanical and dielectric parameters, the materials should have the least possible number of crystalline phases.

All divalent oxides containing relatively small ions (Be^{2+} , Mg^{2+} , Zn^{2+}) and oxides containing ions with a relatively great ionic radius (Cd^{2+} , Ca^{2+} , Sr^{2+} , Pb^{2+} , Ba^{2+}) can be conventionally divided into two groups in accordance with their effect on the dielectric properties.

Oxides of the first group introduced in an alkali-rich glass can at least partially play the role of glass formers; in this position they can polarize and bind the four oxygen ions commonly surrounding them. This weakens the bond between the ions of the alkali metal and the oxygen ions and fixation of the former in the void of the structural skeleton of the glass, which creates the possibility of their free motion under the action of an applied electric field and causes an increase in the dielectric loss tangent.

On the contrary, divalent ions of the second group, usually present in the glass in six coordination, exert a much weaker polarizing effect on each oxygen ion. This creates more favorable conditions for the interaction between the oxygen ions and the alkaline ions and their fixation in the void of the structural skeleton of the glass, which diminishes the dielectric constant [2, 3].

As a result of the conducted study of the effect of strontium and barium oxides on the dielectric properties of lithium aluminosilicate photopyroceraams, we established that the change in these properties agrees with the mentioned theoretical concepts.

We studied the structural changes in lithium aluminosilicate devitrified glasses due to the addition of strontium and barium ions and their effect on the structure, mechanical and dielectric properties of the glasses. Photosensitive devitrified glasses with added Sr^{2+} and Ba^{2+} ions should possess ele-

vated dielectric parameters. The dielectric losses in glass ceramics are mainly caused by migration of ions of the alkali metals that enrich the vitreous phase. The mobility of these ions is affected by the structure of the glass and the presence of cations with large ionic radii that block interatomic voids and hamper migration of ions of the alkali metals.

For this purpose we synthesized strontium- and barium-containing devitrified glasses by introducing (here and below in mole fractions) from 1 to 10% SrO and from 1 to 9% BaO , instead of part of SiO_2 in the initial photosensitive glass containing 68% SiO_2 , 24% Li_2O , 3% K_2O , and 5% Al_2O_3 . All the glasses contained 0.06% AgNO_3 and 0.03% CeO_2 (in excess of 100%) as a photosensitive additive [4].

X-ray diffraction analysis showed that the main crystalline phase in strontium-bearing photosensitive devitrified glasses was lithium metasilicate $\text{Li}_2\text{O} \cdot \text{SiO}_2$ and β -eucryptite $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; the specimen with 10% SrO also contained lithium disilicate $2\text{Li}_2\text{O} \cdot \text{SiO}_2$. Figure 1 presents the electron micrographs of the microstructure of strontium-containing photosensitive devitrified glasses, Table 1 presents their properties.

All strontium-bearing photosensitive devitrified glasses possess a somewhat loose microstructure with a quite high content of vitreous phase. The data from the diffraction analysis confirm this. With an increase in the content of SrO , the amount of crystalline phase diminishes with a corresponding change in the microstructure of the material. The crystal sizes increase with an increase in the content of SrO . The microstructure of specimens containing 8, 9, and 10% SrO is characterized by the segregation of a new phase, possibly, α -eucryptite, the extended prismatic crystals of which attain a size of several micrometers (see Fig. 1f, g, h). In specimens with 7, 8, 9, and 10% SrO_2 , we determined columnar crystals

¹ Ryazan State Pedagogical University, Ryazan, Russia;
Moscow State Open University, Moscow, Russia.

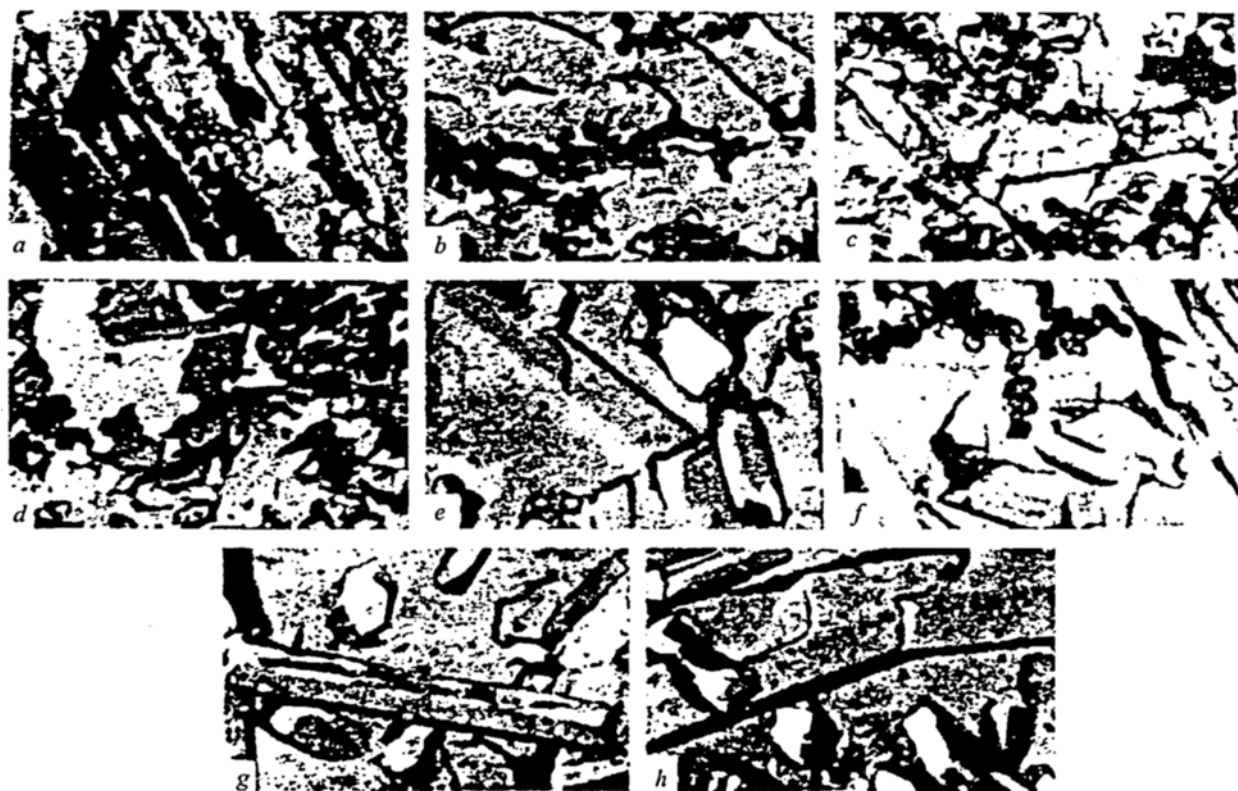


Fig. 1. Electron micrographs of photosensitive devitrified glasses (photopyrocerams) containing 2% (a), 4% (b), 5% (c), 6% (d), 7% (e), 8% (f), 9% (g), and 10% (h) SrO.

of lithium disilicate and poorly discernible acicular crystals of lithium metasilicate, though the presence of this phase was confirmed by the x-ray method.

The introduction of SrO in lithium aluminosilicate photosensitive devitrified glasses causes the formation of a coarse crystalline microstructure. Sr^{2+} ions with a radius of 0.127 nm cannot be positioned either in the vertexes of the tetrahedrons of the structural lattice of β -quartz or in its internal cavities, i.e., they do not enter the composition of quartz-like solid solutions of β -eucryptite and seem to form incompatible crystalline phases, which loosens the microstructure and stimulates the growth of large crystals.

With an increase in the degree of crystallization and a decrease in the content of SrO, the microdistortions of the crystal lattice in strontium-bearing photosensitive devitrified glasses diminish (see Table 1). This can be explained by a certain effect of the anisotropic crystals of β -eucryptite, the content of which increases in the specimens with an increase in the degree of crystallization. It is known that β -eucryptite has strongly manifested anisotropy of the temperature coefficient of linear expansion. For this reason stresses concentrate on the interfaces of the crystal grains and the glass phase and cause microdistortions of the lattice.

TABLE 1

Specimen	Content of SrO, %	Degree of crystallization, %	Size of the region of coherent scattering, nm	Value of microdistortions, 10^3	Dislocation density, 10^{11} cm^{-2}	Dielectric loss tangent at a frequency of 1 MHz and temperature of 20°C , 10^4	Phase composition
S-1	0	60	26	3.0	2.7	77	$\text{Li}_2\text{O} \cdot \text{SiO}_2$, β -eucryptite, α -eucryptite
S-3	2	51	31	2.4	1.6	63	The same
S-5	4	48	30	2.4	1.6	42	The same
S-11	10	33	24	2.0	1.8	20	$\text{Li}_2\text{O} \cdot \text{SiO}_2$, $2\text{Li}_2\text{O} \cdot \text{SiO}_2$, $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$

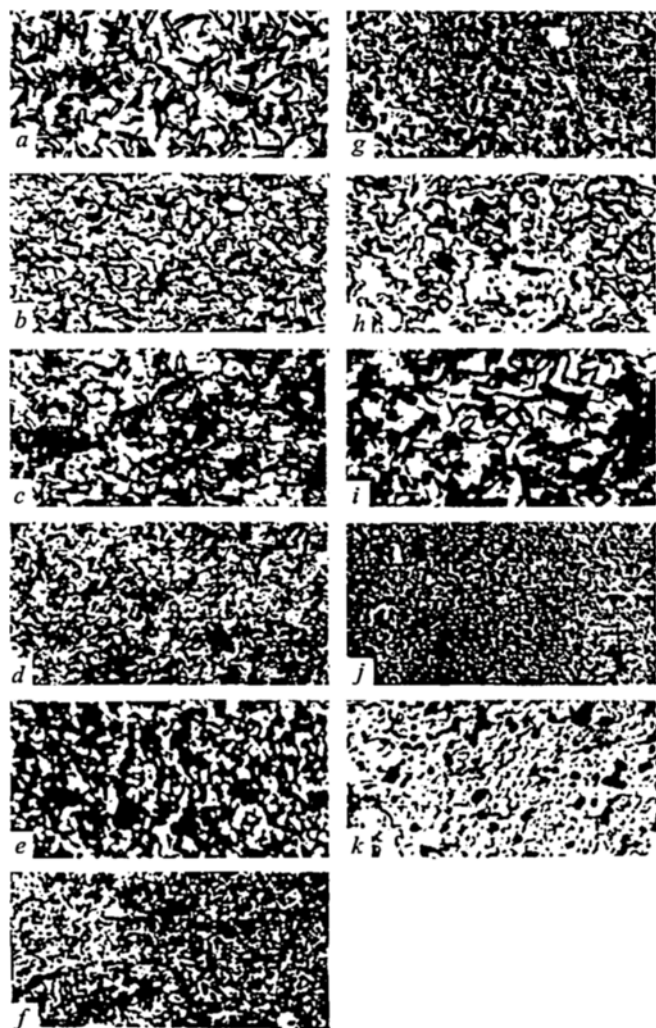


Fig. 2. Electron micrographs of the microstructure of photosensitive devitrified glasses containing 0% (a), 1% (b), 2% (c), 3% (d), 4% (e), 5% (f), 6% (g), 7% (h), 8% (i), 9% (j), and 10% (k) BaO.

The changes in the structure cause changes in the dielectric properties of the photosensitive devitrified glasses. For example, with an increase in the content of SrO and a decrease in the degree of crystallization from 60 to 33%, the dielectric loss tangent diminishes from 77×10^{-4} to 20×10^{-4} . In accordance with the published data, the decrease in the content of the crystalline phase of strontium-containing photosensitive devitrified glasses should worsen the dielectric properties of the materials because the main source of dielectric loss in them is the retained vitreous phase enriched with alkaline ions. The lower the amount of this phase, the less the dielectric loss. However, in our experiments the increase in the content of the vitreous phase was accompanied by a decrease in the dielectric loss tangent rather than an increase. This contradicts the generally accepted concepts on the effect of the vitreous phase on the dielectric properties of a glass ceramic material and requires special consideration.

Since the x-ray phase analysis did not show any strontium-bearing crystalline phase, we assumed that the predominant part of Sr^{2+} ions with a large ionic radius (0.127 nm) is contained in the vitreous phase and blocks effectively the motion of the alkaline ions. The latter can cause a decrease in the dielectric loss of the material with an increase in the content of SrO_2 in it despite the decrease in the degree of crystallization (increase in the amount of vitreous phase). Thus, photosensitive devitrified glasses with added ions having a large ionic radius, specifically, Sr^{2+} , should possess elevated dielectric characteristics relative to the initial material.

Such an interpretation of our results agrees well with the data known from published sources.

In [5] we conducted an x-ray phase study and electron microscopic analysis of lithium aluminosilicate photosensitive devitrified glasses with from 1 to 9% BaO additive and a corresponding decrease in the content of SiO_2 . With the introduction of BaO instead of SiO_2 , we expected a change in the phase composition and a corresponding change in the mechanical and dielectric properties of the materials. The introduction of barium oxide with an ionic radius greater than that of the strontium ion, the dielectric characteristics of the photosensitive glass should be improved.

Table 2 presents the results of a study of the phase composition, the dislocation density, the dielectric and mechanical properties of barium-bearing photosensitive devitrified glasses, Fig. 2. presents micrographs of their chips, and Figs. 3 and 4 present the dependences of the dislocation densities, the degree of crystallization, and the sizes of regions of coherent scattering on the content of BaO.

The x-ray phase analysis of glasses with various contents of BaO showed that they commonly contained 4–5 crystalline phases. The main crystalline phase was lithium metasilicate $\text{Li}_2\text{O} \cdot \text{SiO}_2$ and quartz-like solid solutions of α - and β -eucryptite $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ plus hexacelsian $\beta\text{-BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Barium-bearing photosensitive devitrified glasses possessed a fine crystal structure with crystals less than 0.1 μm in size.

The segregation of these crystalline phases was confirmed by the electron microscopic study (see Fig. 2). The micrographs of specimens with addition of 1, 2, 6, and 7% BaO exhibited acicular crystals of lithium metasilicate. In specimens with 8, 9, and 10% BaO, we determined fine-grain aggregates of β -eucryptite. Columnar crystals of lithium disilicate can be seen in the glass with 7–8% BaO. The Ba^{2+} ion has a greater radius (0.143 nm) than the Sr^{2+} ion (0.127 nm). This should have caused larger crystal sizes, but the formation of a fine crystal structure in barium-bearing photosensitive devitrified glasses is a consequence of the high photosensitivity of the initial glasses.

We established that barium-bearing glasses possess high photosensitivity that increases with the content of BaO. For example, in glasses with 8–10% BaO, the difference in the temperatures of the beginning of crystallization in irradiated

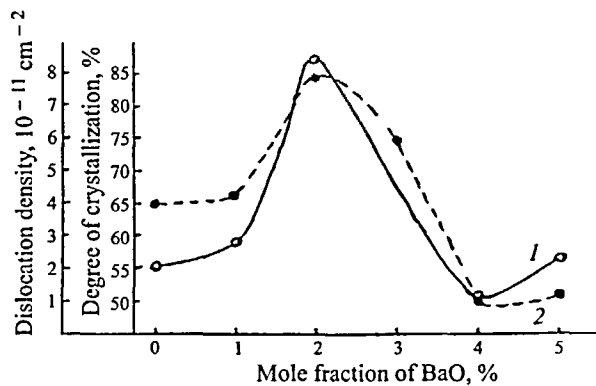


Fig. 3. Dependence of the dislocation density (1) and degree of crystallization (2) of lithium aluminosilicate photosensitive devitrified glasses on the content of BaO.

and nonirradiated regions ranged between 115 – 125°C versus 30 – 50°C in the initial glasses without the BaO additive.

We established that there is some correlation between the parameters of the fine structure, the mechanical, and dielectric properties of the barium-containing photosensitive devitrified glasses. For example, the maximum degree of crystallization (85%) and elevated dislocation density ($8.6 \times 10^{11} \text{ cm}^{-2}$) corresponded to the minimum microhardness (6.3 GPa) and diminished dielectric loss (60×10^{-4}). The dense microstructure with a low content of amorphous phase provided for high hardness. In addition, in accordance

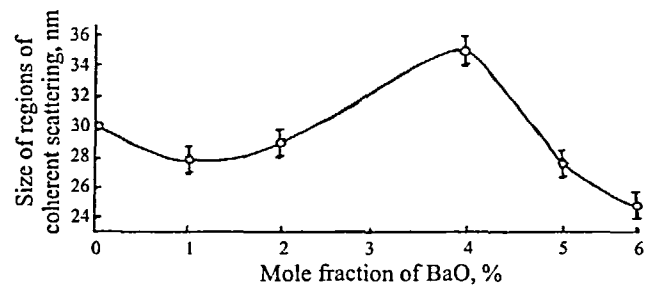


Fig. 4. Dependence of regions of coherent scattering in photosensitive devitrified glasses on the content of BaO.

with the theory of dislocations [6] a material with a high dislocation density should possess high mechanical characteristics.

The fact that the maximum degree of crystallization corresponded to the highest dislocation density in the specimen with 2% BaO can be explained by the fact that dislocations accumulate predominantly on grain (crystallite) boundaries where the crystal lattice is distorted the least. The length of the grain boundaries should be greatest in the specimen with the maximum degree of crystallization (85%). This causes greater accumulation of dislocations [7].

The marked decrease in the dielectric loss tangent from 81×10^{-4} to $(9 - 10) \times 10^{-4}$ in glasses with up to 9% BaO can be explained by the fact that the Ba^{2+} ion with a radius of 0.143 nm can enter not only the crystalline phase of hexacelsian, but also the retained vitreous phase. This diva-

TABLE 2

Specimen	Content of BaO, %	Degree of crystallization, %	Size of the region of coherent scattering, nm	Value of microdistortions, 10^3	Dislocation density, 10^{11}	Vickers microhardness, GPa	Dielectric loss tangent at a frequency of 1 MHz and temperature of 20°C, 10^4	Phase composition
Ba-1	0	65	30	2.2	2.1	5.0	81	$\text{Li}_2\text{O} \cdot \text{SiO}_2$, β -eucryptite, α -eucryptite, $2\text{Li}_2\text{O} \cdot 2\text{SiO}_2$
Ba-2	1	67	28	1.8	2.8	5.4	81	The same
Ba-3	2	85	29	2.0	8.6	6.3	60	The same
Ba-4	3	75	Not determined			5.6	10	$\text{Li}_2\text{O} \cdot \text{SiO}_2$, β -eucryptite
Ba-5	4	50	35	1.5	1.2	4.9	26	$\text{Li}_2\text{O} \cdot \text{SiO}_2$, β -eucryptite, $2\text{Li}_2\text{O} \cdot 2\text{SiO}_2$
Ba-6	5	53	28	2.0	2.6	4.9	20	$\text{Li}_2\text{O} \cdot \text{SiO}_2$, β -eucryptite, $2\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, hexacelsian
Ba-7	6	84	25	0.7	4.0	5.6	Not determined	$\text{Li}_2\text{O} \cdot \text{SiO}_2$, β -eucryptite, $2\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, α -eucryptite, hexacelsian
Ba-8	7	70	Not determined			5.2	11	$\text{Li}_2\text{O} \cdot \text{SiO}_2$, β -eucryptite, hexacelsian
Ba-9	8	73	The same			6.1	40	$\text{Li}_2\text{O} \cdot \text{SiO}_2$, β -eucryptite, $2\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, hexacelsian
Ba-10	9	74	The same			5.6	9	$\text{Li}_2\text{O} \cdot \text{SiO}_2$, β -eucryptite, hexacelsian

lent barium ion is commonly present in the glass in six coordination. Due its large radius, it exerts a small polarizing action on each oxygen ion, creating favorable conditions for interaction between the oxygen ions and the ions of the alkali metal and their fixation in the void of the structural lattice of the glass, which restrains the motion of the alkaline ions and diminishes the dielectric loss tangent.

Based on the analysis of the experimental data, we made a conclusion that in order to obtain a homogeneous compact microstructure, high mechanical properties and dielectric parameters in photosensitive devitrified glasses, we should attempt to fabricate a material with the least possible number of phases.

The maximum size of the regions of coherent scattering that amounted to 35 nm was observed in the glass with 4% BaO, which corresponded to a low degree of crystallization (50%) of the specimen. The specimen with the largest regions of coherent scattering had a large layer of vitreous phase. The dislocation density in this specimen was minimum ($1.2 \times 10^{11} \text{ cm}^{-1}$).

The first traces of plastic deformation in polycrystalline materials should appear over the boundaries of the crystallites and the limit of elasticity should be very sensitive to the size of the crystallites and increase with a decrease in them [6]. It follows that the microhardness of a photosensitive devitrified glass should also depend on the dislocation density. For example, in the specimen with the minimum dislocation density, we should expect worsening of the mechanical properties. The microhardness of this specimen (4.9 GPa) was lower than in other specimens of barium-containing glass. This agrees with the published data (Patent USA 3282712) for pyrocerams of spodumene composition, the

microhardness of which diminishes with an increase in the grain size.

A comparison of the physicochemical and dielectric properties of barium- and strontium-bearing glasses showed that BaO additives provide for better dielectric parameters than SrO additives. This is caused by the difference in the sizes of the Ba^{2+} and Sr^{2+} ions.

Thus, photosensitive devitrified glasses with a homogeneous compact microstructure and high physicochemical and dielectric properties can be obtained by reducing the number of crystalline phases to a minimum.

REFERENCES

1. O. V. Mazurin, *Electrical Properties of Glass* [in Russian], Lengoskhimizdat, Leningrad (1962).
2. D. Stevels, *Electrical Properties of Glass* [Russian translation], Inostrannaya Literatura, Moscow (1961).
3. P. W. Macmillan, "Electrical properties of glass-ceramics," *Sci. Technol.*, **37**(1), 25 – 33 (1970).
4. A. I. Berezhnoi, V. I. Ivanova, A. S. Krasnikov, and M. D. Krasnikova, "A study of the structure and properties of strontium-containing lithium aluminosilicate photosensitive devitrified glasses," *Dokl. Akad. Nauk SSSR*, **205**(6), 1335 – 1338 (1972).
5. A. I. Berezhnoi, V. I. Ivanova, A. S. Krasnikov, M. D. Krasnikova, "A study of the dislocation structure and properties of barium-containing lithium aluminosilicate photosensitive devitrified glasses," *Dokl. Akad. Nauk SSSR*, **209**(6), 1381 – 1384 (1973).
6. I. A. Oding, *The Theory of Dislocations in Metals and Its Applications* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1959).
7. N. M. Pavlushkin and R. Ya. Khodakovskaya, "Devitrified glasses: novel polycrystalline materials based on glass," *Zh. VKhO D. I. Mendeleeva*, **8**(2), 142 – 151 (1968).